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(71) Applicant *(for all designated States except US):* TSL GROUP PLC [GB/GB]; P.O. Box 6, Wallsend, Tyne and Wear NE28 6DG (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : ALLEN, Joseph, Ignatius, Henry [GB/GB]; 55 North Road, Ponteland, Newcastle-upon-Tyne NE20 9MN (GB). SAYCE, Ian, George [GB/GB]; 21 Crabtree Road, Stockfield, Northumberland NE43 7NX (GB). WINTERBURN, John, Alexander [GB/GB]; 7 Ellesmere Gardens, Tynemouth, North Shields NE30 3BE (GB).

(74) Agent: NEWBY, John, Ross; J.Y. & G.W. Johnson, Furnival House, 14-18 High Holborn, London WC1V 6DE (GB).

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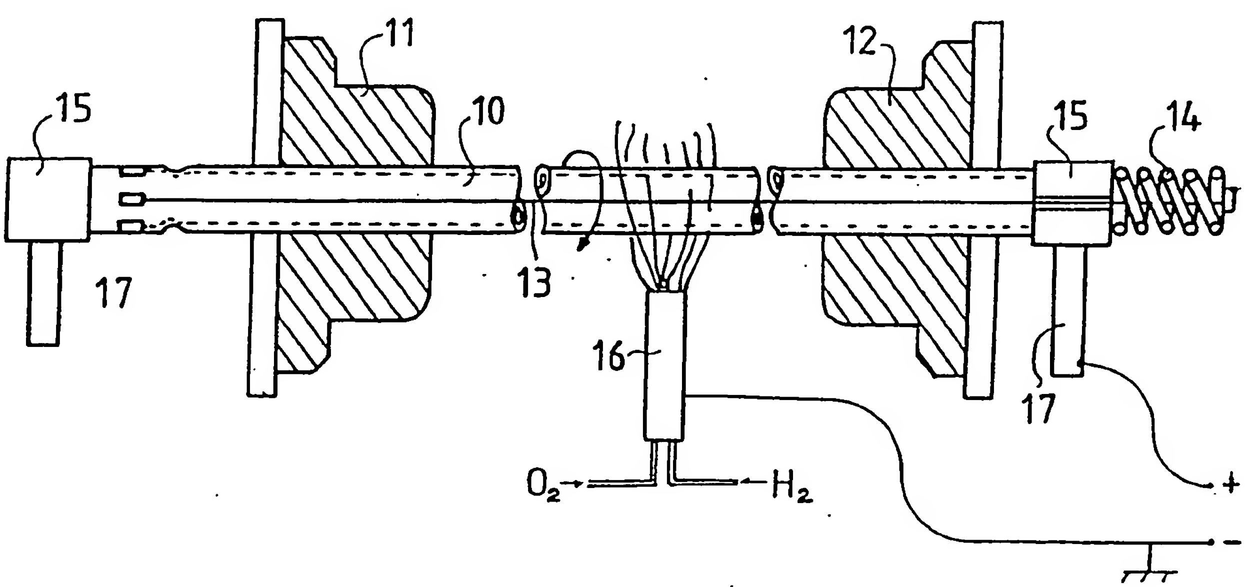
(54) Title: VITREOUS SILICA ARTICLES



(57) Abstract

A method of enhancing the purity of a body (10) of fused quartz comprising maintaining the body at a temperature of at least 1000°C and applying a polarising potential across opposed boundary surfaces of the body, wherein each electrode for applying said polarising potential is gaseous and at least partially ionised.

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VITREOUS SILICA ARTICLES

Technical Field

This invention relates to a method of enhancing the purity of a body of fused quartz, e.g. vitreous silica, having opposed boundary surfaces, the method being of the kind comprising maintaining the body at a temperature above 1000°C while a polarising potential is applied across the said boundary surfaces by means of electrodes in contact with the boundary surfaces so that at least some of the residual impurity ions are made to migrate away from one boundary surface towards the opposite boundary surface thereof and are subsequently discharged into the gaseous phase at the latter boundary surface. In particular the invention is concerned with an electrical purification method and articles purified by the method.

Background Art

High purity vitreous silica (fused quartz) articles are commonly made by flame or electrical fusion of carefully refined powders derived from natural quartz crystal. With increasing attention being paid to residual impurities by certain industries, e.g. semiconductor and optical fibre manufacture, the level of purities sought is at times beyond that which can be achieved by conventional chemical and physical refinement techniques. There may even be an undesirable concentration of alkali ions, in articles manufactured from synthetic quartz or amorphous silica powders, either derived from the starting material or introduced accidentally as contamination in the manufacturing process.

For achieving very low levels of certain mobile metal ion impurities, notably ions of the alkali metals, e.g. lithium, sodium, potassium and copper, the application of

an electrical polarising potential across the wall of a heated quartz article has been proposed (GB-A-2166434). This can effect migration of the impurity ions away from one of the wall surfaces, and toward the opposite wall surface. The article may subsequently be cooled to ambient temperature while the polarising potential is still applied, in which case the impurities accumulating near the cathodic wall surface may be removed by machining or etching off a thin layer at that surface to leave the remaining mass of vitreous silica of higher average purity.

In one example included in the above-noted patent application, a method was described in which a vitreous silica crucible was inverted over an internal graphite mould and the crucible was rotated slowly while being heated with an oxy-propane burner. An electric potential of 4.5 kV was applied with the mould serving as negative electrode and the burner flame as positive electrode. Significant depletion of alkali metal ions was observed in the inner layers of the crucible, but while some coloration was observed in the flame due to the release of ions electrolysed from the crucible into the gas flame, significant amounts of alkali metal remained in the outer layers of glass.

The present invention represents an advance on the prior art and while it has several applications, it is particularly suited to the manufacture of fused quartz tubing, crucibles, and other hollow ware. The method of the invention may be applied to a finished tube or hollow ware, or in the course of drawing of the tube, or manufacture of the hollow ware or both during and after manufacture.

Summary of the Invention

According to the present invention a method of the kind referred to of enhancing the purity of a body of fused quartz having opposed boundary surfaces, is characterised

in that each of the electrodes is gaseous and at least partially ionised.

Whereas in the past one or both of the electrodes used for electrolysing fused quartz has been a solid in contact with a surface of the fused quartz, it has now been found that it is possible to effect purification of a mass of heated fused quartz, for example a tube, by non-contact means using hot conductive gas flows to serve as both positive and negative electrodes. This is particularly important in the purification of tubing for fibre optic applications, where any solid contact with the hot tube could cause unacceptable contamination or surface deformation.

It has furthermore been discovered that by using a hot conductive gas flow as the cathode, or negative electrode, and by ensuring that the cathodic surface of the mass of fused quartz is maintained at a sufficiently high temperature in a purging flow of gas, then it is possible to effect extensive volatilisation of the mobile impurity cations which would otherwise accumulate at the cathodic surface. Although the method according to the invention can be operated with the body of fused quartz at a temperature of 1000°C, it proceeds increasingly rapidly with higher temperatures, the preferred range being from 1500°C to 2100°C. The rate of movement of impurity ions towards the said opposite boundary surface is also dependent on the polarising potential applied and a potential difference of at least 10 V/mm thickness across the boundary surfaces is considered to be the minimum practical value.

The best known mobile impurities in vitreous silica are the ions of the alkali metals and of copper which may thus be substantially removed from a fused quartz article without the need for any solid contact with either surface of the article.

Brief Description of the Drawings

Figure 1 is a partly sectioned schematic view of one embodiment of apparatus for performing a method according to the invention of enhancing the purity of a fused quartz tube,

Figure 2 is a sectional view of another embodiment of apparatus for performing a method according to the invention of enhancing the purity of a tubular article of fused quartz, and

Figure 3 is a sectional view of a further embodiment of apparatus for performing a method according to the invention of enhancing the purity of a fused quartz crucible.

Description of Preferred Embodiments

Various methods according to the invention of enhancing the purity of bodies of fused quartz are illustrated by the following examples which should be read with reference to the appropriate one of the accompanying drawings.

Example 1 (see Figure 1)

A fused quartz tube 10 of outside diameter 25 mm and inside diameter 19 mm was mounted between the chucks 11,12 of a glass-working lathe. A wire 13 (e.g. of tungsten or molybdenum) was threaded through the tube bore and supported under slight tension along the tube axis by a spring 14. Gas fittings 15 and seals were provided in the tube bore so that argon gas (at a flow rate of 5 L/min) could be passed through the tube 10 while the latter was rotated in the lathe.

While thus rotating, the tube was heated by a metal oxy-hydrogen burner 16 (e.g. a semi-circular burner) to a

temperature of 1600°C, determined by the flow of gases and the rate of traverse of the burner in the axial directions of the tube.

While the burner was traversed along the tube at a rate of 50 mm/minute, a potential of 3.5 kV was applied between the wire 13 as anode (positive electrode) via graphite brushes 17 and the metal burner 16 as cathode (negative electrode). A corona discharge was observed within the tube bore around the wire 13 in the hot zone. The argon flow within the tube bore both protected the wire 13 and also provided a conductive path for the electrolysing current, (50 mA).

On application of the electrical potential a bright orange glow was observed in the burner flame which thus provided a conductive gaseous electrical contact with the exterior of the tube. Mobile metallic impurity ions were thus caused to diffuse through the fused quartz to the outer surface wall of the tube, where the hot gases stimulated vaporisation of the impurity ions, at the zone of impingement of the flame with the external surface of the tube.

The above treatment permitted a substantial up-grading of the purity of the tube material with respect to the following mobile metal ions, lithium, sodium, potassium and copper, as demonstrated by the analytical results below (ppm by weight).

	Typical Starting Tube	Similar Tube after Treatment
Li	0.34	< 0.01
Na	0.45	< 0.01
K	0.11	< 0.01
Cu	0.01	< 0.01

Example 2 (see Figure 2)

A hollow cylindrical ingot 20 of fused quartz having a wall thickness of 45 mm was lowered through a high temperature graphite furnace 21, as conventionally used for redrawing an annular ingot to tubing, operating at a temperature of 2100°C. The interior 22 of the furnace was purged with nitrogen, and this gas surrounded the ingot providing a gaseous conductive path between it and the graphite furnace.

In the course of the redrawing process, a graphite bobbin 23 was lowered on a graphite cord 24 down the axis of the annular ingot 20 through the furnace hot zone. An atmosphere of argon was maintained within the ingot, to preserve the graphite parts and to provide a conductive path for the electrolysis current.

A potential of 1000 volts was maintained between the graphite cord 24 as anode, and the graphite furnace 21 as cathode, and a current of 0.6 amps was caused to flow.

An electrolytic purification of the fused quartz occurred in the course of the above redrawing process, as is shown by the analytical figures given below. Once again the impurities are expressed in ppm by weight

	Tube without Electrolytic Current	Tube following Electrolytic Purification
Li	0.4	< 0.01
Na	0.54	< 0.01
K	0.20	< 0.01

Variations of the above process will be readily apparent to those skilled in the art.

Thus electrolytic purification in a lathe could be effected using either burner or plasma torch as heat source or gaseous electrode, alternatively a graphite or similar external furnace surrounding the tube in whole or in part could be employed.

The inner electrode could be replaced with a small internal burner, or plasma jet, or by alternative means of conduction, and the electrical polarity of the system may be reversed if required.

Again, the use of electrolytic purification in the course of redrawing of a larger ingot of fused quartz to a smaller sized product can be effected with alternative anode/cathode configurations, or the furnace may be replaced or supplemented by a flame or plasma heat source/electrode. Again the polarity of the system may be reversed if required.

Example 3 (see Figure 3)

A fused quartz crucible 30 having a wall thickness of 9 mm was inverted and placed over but not in contact with a hollow high purity graphite internal mould 31; the gap 32 between the mould 31 and the inner surface of the crucible 30 was uniformly about 5 mm.

The crucible and graphite were slowly rotated under an arrangement of ribbon flames 33 created by a water-cooled metal burner 34 fed with fuel gas and oxygen, and the crucible 30 was heated to a temperature of (about) 1500°C. A voltage of 2 kV was applied, between the burner 34 and the mould 31 such that the graphite mould 31 formed the anode and the metal burner 34 and its array of flames 33 formed the cathode of the electrolytic circuit. A current of 160 mA was caused to flow, and the flame was seen to glow bright orange.

The interior 35 of the mould 31 is filled with argon to serve as a protective atmosphere.

After this treatment, the crucible 30 was found to have a substantially reduced alkali content, as shown in the results below.

	Typical crucible untreated	Crucible after treatment
Li	0.4	< 0.01
Na	0.3	< 0.01
K	0.6	0.01
Cu	0.02	< 0.01

all in parts per million by weight

Again, this Example demonstrates the efficiency of electrolytic purification, whereby both anodic and cathodic connections to the quartz are gaseous, and the mobile metal ion impurities may be volatilised at the cathodic surface.

The method of the invention operates conveniently at atmospheric pressure, but operation at higher or lower pressure is feasible. While argon represents a convenient conductive gas for use within a hollow tube or ingot being electrolysed, other gases may be used provided they yield a suitably conductive path under the conditions of temperature and pressure chosen for operation. In principle, any gas could be used to comprise the gaseous electrode, but it is preferable to employ a gas which is readily used, non-hazardous, and does not react deleteriously with any components in the system. The so-called inert gases may be conveniently employed as can nitrogen or hydrogen. Other gases or gas mixtures may also be used.

As noted above, a combustion flame may likewise provide a useful source of conductive gas to act as one or both electrodes in the system. Such combustion flames may

typically be generated by any appropriate fuel gas-oxidant combination. The combination in air, or preferably oxygen, of one or more of the fuel gases hydrogen, methane, ethane, propane, butane or acetylene, may be conveniently utilised in the present application.

Radial flow of electrolytic current, and therefore ion diffusion is obviously preferred, but depending on the geometry of the article being purified, other geometrical arrangements of electrode and workpiece may be used if required. An arrangement of particular interest is that of a quartz glass plate, whereby it is possible to achieve electrolytic purification of at least the central regions of a plate of fused quartz by traversing the plate between a pair of gaseous electrodes as defined above, for example a pair of oxy-hydrogen ribbon burners may be employed, both to heat the plate and to provide the necessary conductive gas flows.

CLAIMS

1. A method of enhancing the purity of a body of fused quartz having opposed boundary surfaces, comprising maintaining the body at a temperature above 1000°C while a polarising potential is applied across the said boundary surfaces by means of electrodes in contact with the boundary surfaces so that at least some of the residual impurity ions are made to migrate away from one boundary surface towards the opposite boundary surface thereof and are subsequently discharged into the gaseous phase at the latter boundary surface, characterised in that each of the electrodes is gaseous and at least partially ionised.

2. A method as claimed in claim 1, characterised in that the polarising potential is poled to make alkali metal ions and copper ions migrate away from said one boundary surface and be discharged into the gaseous phase at said opposite boundary surface.

3. A method as claimed in claim 1 or 2, characterised in that the body is heated to said temperature above 1000°C by a flame, an electric arc, a plasma jet or a furnace.

4. A method as claimed in any one of the preceding claims, characterised in that the fused quartz body is a crucible, a hollow cylinder or a plate.

5. A method as claimed in any of claims 1 to 3, characterised in that the fused quartz body is a hollow cylinder and the purity enhancement is undertaken during re-shaping of the hollow cylinder to form a body of differing diameter or cross-sectional area.

6. A method as claimed in any one of the preceding claims, characterised in that the body is maintained for a time corresponding to the thickness of the wall being

polarised of at least 10 seconds/mm in the temperature range 1500°C to 2100°C and the effective polarising potential applied across the said boundary surfaces exceeds 10 V/mm thickness.

7. A method as claimed in any one of the preceding claims, characterised in that at least one of the gaseous electrodes is connected to electrical circuitry via a refractory conductor made from metal or carbon.

8. A method as claimed in any of the preceding claims, characterised in that the gaseous electrodes used to apply the polarising voltage are chosen from ionised helium, argon, neon, krypton, xenon, nitrogen or hydrogen or the flame produced by the combustion of hydrogen, methane, propane, butane or acetylene.

9. A fused quartz body, characterised in that its purity has been enhanced by the method claimed in any one of the preceding claims.

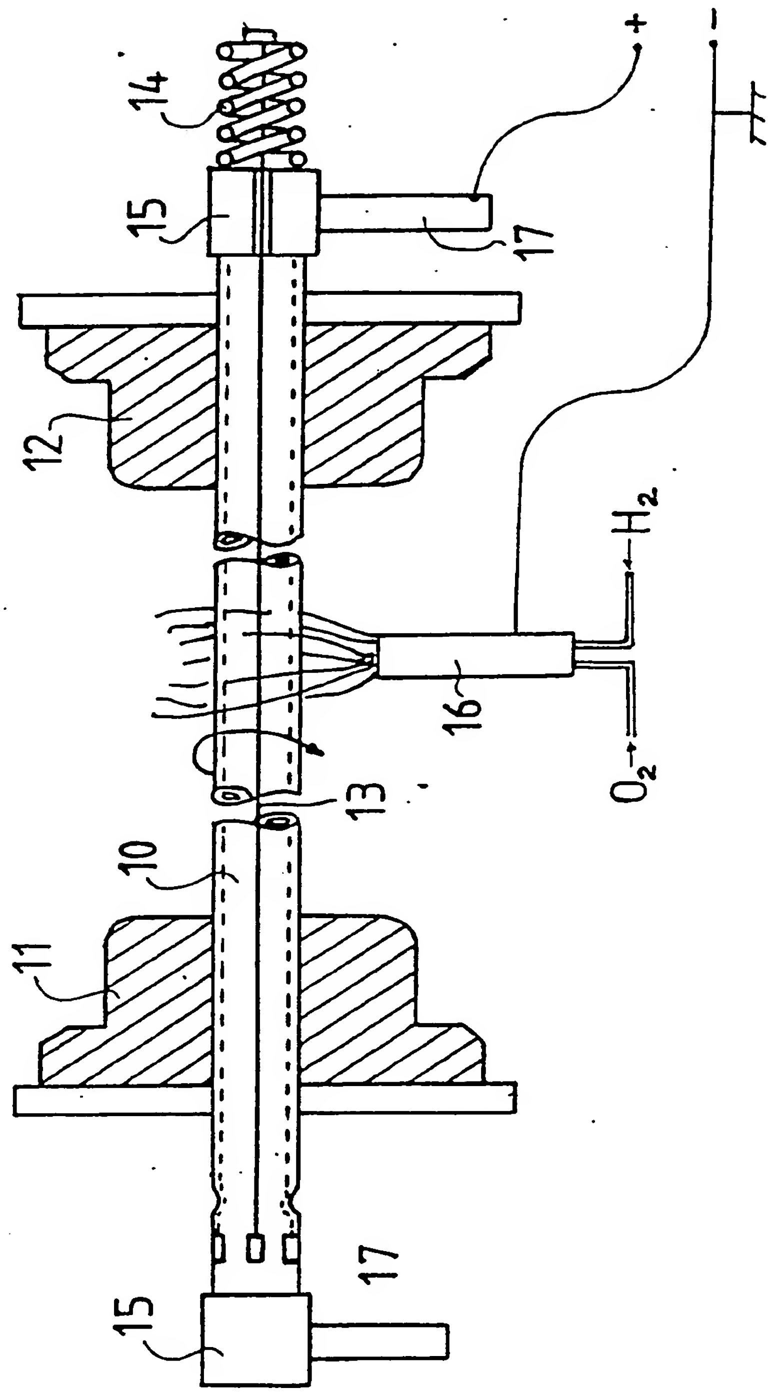


FIG. 1

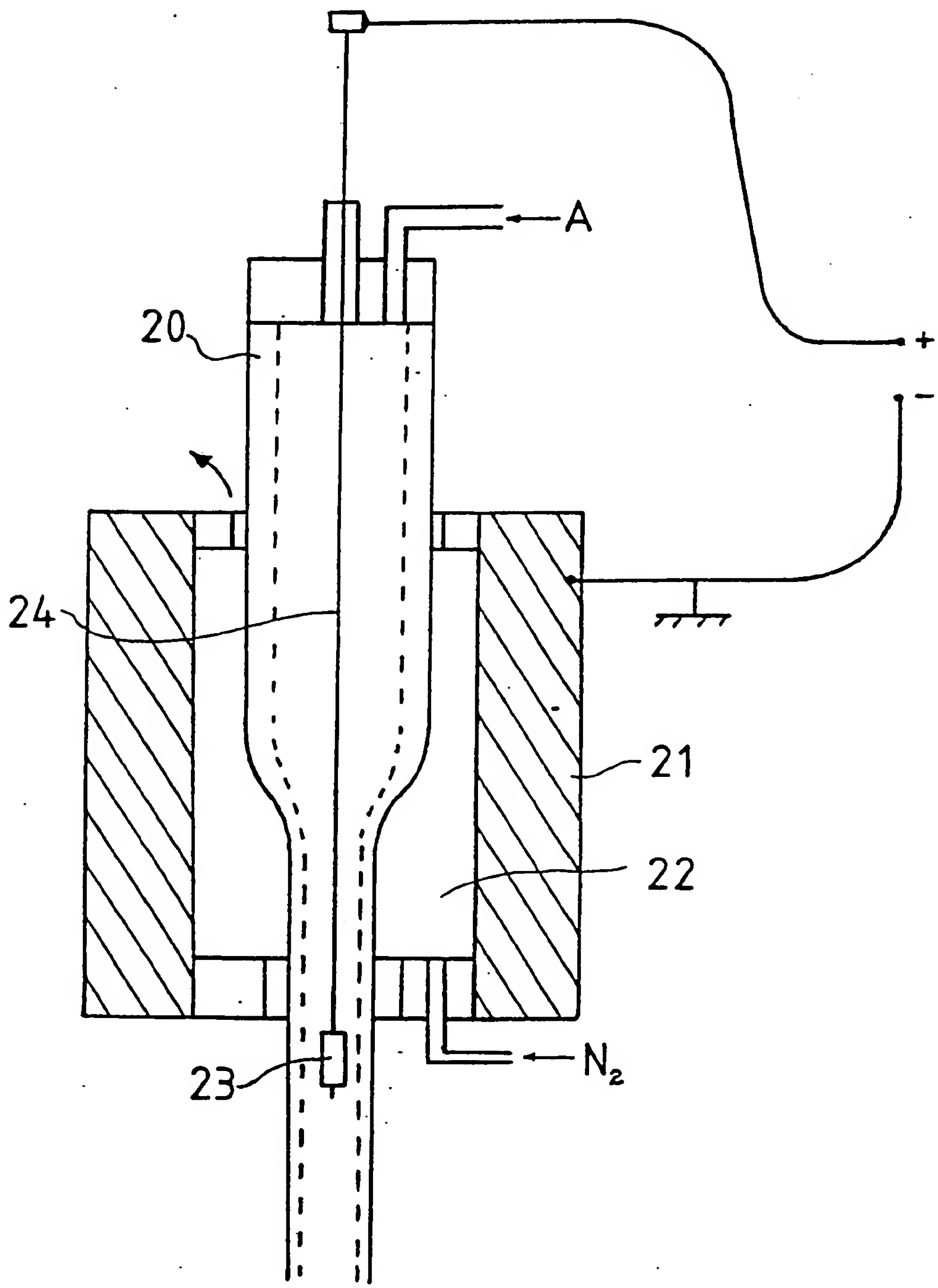
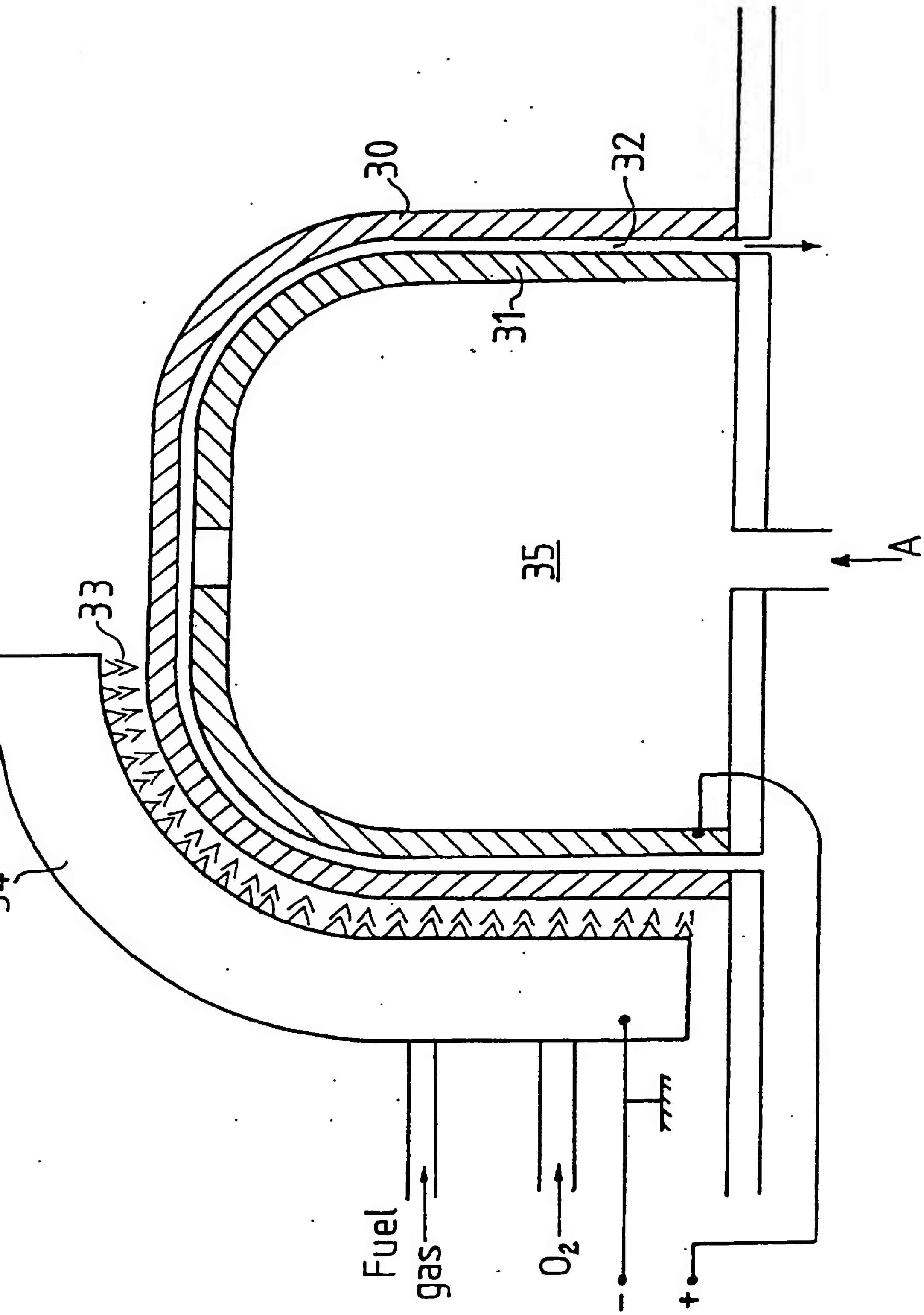


FIG. 2

FIG. 3



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 89/00960

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: C 03 C 23/00, C 03 B 32/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	C 03 C, C 03 B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	WO, A, 86/02919 (TSL THERMAL SYNDICATE PLC) 22 May 1986 see example 7; figure 4; claims 1,4, 13-16; page 4, lines 12-31 cited in the application --	1-9
A	EP, A, 0237431 (SAINT-GOBAIN VITRAGE) 16 September 1987 see claims 1,6-9,11,13 --	1-4,7-9
A	Patent Abstracts of Japan, volume 9, no. 21 (C-263)(1744), 29 January 1985, & JP, A, 59169956 (SUWA SEIKOSHA K.K.) 26 September 1984 see the abstract	1,4,9

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
21st November 1989	[illegible] 12. 89
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EUROPEAN PATENT OFFICE	T.K. WILLIS

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP-T- 62501067	30-04-87
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		US-A- 4824458	25-04-89

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